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**(54) MANUFACTURE OF UNSATURATED NITRILE****(57) Abstract:**

**PURPOSE:** To manufacture acrylonitrile or methacrylonitrile at high yield by using a catalyst which is modified by adding specific metal to a conventional catalyst containing Mo, Bi and iron.

**CONSTITUTION:** Acrylonitrile or methacrylonitrile is manufactured by bringing propylene or isobutylene into contact with ammonia and oxygen in a gas phase at high temperature in the presence of a catalyst. In this case, the catalyst used consists of 40 to 60wt.% silica that carries the composition shown by the formula (Q is at least one kind of element selected from Cr and In; A is at least one kind of element selected from K, Rb and Cs; E is at least one kind of element selected from Mn, Mg, Zn, Ce, Na And P; (m), (b), (f), (n), (q), (a), (l) and (x) indicate atomic ratios; m=10 to 14, b=0.1 to 3, f=0.1 to 3, n=4 to 10, q=0.1 to 2, a=0.01 to 0.5, l=0 to 3; and (x) is the atomic ratio oxygen corresponding to the oxide of a metal component in the composition).

**Mo ■ Bi b F e f N i n Q q A a E e O x**

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*\*Translation Editor's Note: We have included the extremely minor revisions listed at the end of the foreign, directly into our translation.*

(54) [Title of the Invention]

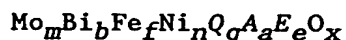
METHOD FOR THE PRODUCTION OF UNSATURATED NITRILES

(57) [Abstract]

[Object] To provide a method for the production of acrylonitrile or methacrylonitrile in high yield using an improved conventional catalyst.

[Constitution] The invention method uses a catalyst as represented by the following general formula, which is composed of molybdenum, bismuth, iron, and specific metals, in the ammoxidation of propylene or isobutylene.

[Formula 1]

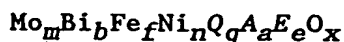


(in which Q is chromium or indium; A is potassium, rubidium, or cesium; and E is manganese, magnesium, zinc, cerium, sodium, or phosphorus).

[Scope of the Patent Claim(s)]

[Claim 1] Method for the production of acrylonitrile or methacrylonitrile, characterized in that in the preparation of acrylonitrile or methacrylonitrile by the vapor-phase contact of propylene or isobutylene with ammonia and oxygen at a high temperature in the presence of a catalyst, a catalyst is used which is prepared by deposition on 40-60 wt.% of silica of a composition which can be represented by the following general formula:

[Formula 1]



(in which Mo is molybdenum, Bi is bismuth, Fe is iron, Ni is nickel; Q is at least one element selected from chromium and indium; A is at least one element selected from potassium, rubidium, and cesium; E is at least one element selected from manganese, magnesium, zinc, cerium, sodium, and phosphorus; O is oxygen; m, b, f, n, q, a, e, and x are atomic ratios; where m = 10-14, b =

0.1-3,  $f = 0.1-3$ ,  $n = 4-10$ ,  $q = 0.1-2$ ,  $a = 0.01-0.5$ ,  $e = 0-3$ , and  $x$  is the atomic ratio of oxygen corresponding to the oxides of the metal constituents in the general formula).

[Claim 2] Method according to Claim 1, characterized in that  $E$  is at least one element selected from zinc and cerium.

[Claim 3] Method according to Claim 2, characterized in that  $Q$  is a mixture of chromium and indium.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The present invention pertains to a method for the preparation of acrylonitrile or methacrylonitrile by the vapor-phase contact of propylene or isobutylene with ammonia and oxygen in the presence of a multifunctional oxide catalyst that contains molybdenum, bismuth, and iron.

[0002]

[Prior Art Technology] Method for the production of acrylonitrile or methacrylonitrile by the vapor-phase oxidation of propylene or isobutylene by molecular oxygen in the presence of ammonia is widely known as the "ammoxidation process" and it is presently being used on an industrial scale. Many catalysts that contain molybdenum, bismuth, and iron and that are used in this reaction appear in the literature. For example, multicomponent oxide catalysts that contain molybdenum, bismuth, and iron are disclosed in Japanese Kokai Nos. 2[1990]-59,046 and 2[1990]-251,250, Japanese Kokoku Nos. 40[1965]-2,532, 50[1975]-15,773, 51[1976]-6,649, 52[1977]-45,692, 59[1984]-50,667, 60[1985]-36,812, and 62[1987]-42,654, and U.S. Patents Nos. 4,167,494 and 5,093,299.

[0003] These are excellent catalysts that offer various advantages, however there is a lack of control over the ammoxidation side reactions and the yield of desired product is unsatisfactory.

[0004]

[Problems to be Solved by the Invention] The object of the present invention is to provide a method for the preparation of acrylonitrile or methacrylonitrile in higher yields by the use of an improved conventional catalyst.

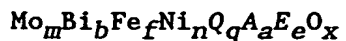
[0005]

[Means for Solving the Problems] The essential feature of the method according to the invention is to catalyst itself. As a result of various studies carried out by the present inventors on catalysts that contain molybdenum, bismuth, and iron for the ammoxidation of propylene or isobutylene, it was found that an oxide which is a composite of these components plus specific metal component(s) could further increase the yield of acrylonitrile or methacrylonitrile, and this discovery led to the development of the present invention.

[0006] The invention catalysts are prepared by deposition on 40-60 wt.% of silica of a composition which can be represented by the following general formula:

[0007]

[Formula 2]



(in which Q is at least one element selected from chromium and indium; A is at least one element selected from potassium, rubidium, and cesium; E is at least one element selected from manganese, magnesium, zinc, cerium, sodium, and

phosphorus;  $m$ ,  $b$ ,  $f$ ,  $n$ ,  $q$ ,  $a$ ,  $e$ , and  $x$  are atomic ratios of molybdenum, bismuth, iron, nickel, component Q, component A, component E, and oxygen, respectively; where  $m = 10-14$ , and preferably  $11-13$ ;  $b = 0.1-3$ , and preferably  $0.3-2$ ;  $f = 0.1-3$ , and preferably  $0.5-2.5$ ;  $n = 4-10$ , and preferably  $5-9$ ;  $q = 0.1-2$ , and preferably  $0.2-1.5$ ;  $a = 0.01-0.5$ , and preferably  $0.1-0.4$ ;  $e = 0-3$ ; and  $x$  is the atomic ratio of oxygen that satisfies the valences of the metal components in the general formula).

[0008] The catalyst of the present invention is characterized in that it contains the essential component Q which enhances the effective action and characteristics of the catalyst. For example, when a mixture of chromium and indium (component Q) is used, a better yield of acrylonitrile or methacrylonitrile can be obtained than when only chromium or only indium is used. When chromium alone is used, it is advisable for  $q$  to be less than one. The preferred amount of Q is such that the relative amount of Q with respect to iron, i.e.,  $q/(q + f)$  is 0.7 or less.

[0009] In the catalyst of the present invention, the essential component A, of which a very small amount is used, improves the selectivity for acrylonitrile or methacrylonitrile. With regard to component A, in case rubidium or cesium is used alone in a smaller amount than that of potassium, the selectivity for acrylonitrile or methacrylonitrile will be improved. If the amount of component A used is outside the range specified in the present invention, propylene or isobutylene reactivity will be decreased.

[0010] An arbitrary component C can be suitably selected and used to adjust the reactivity and physical properties of the catalyst. For example, phosphorus can be used as component C to improve the wear resistance of the catalyst.

[0011] Silica serves as the catalyst support. The silica-supported catalyst of the present invention shows excellent fluidity when used in a fluidized-bed ammoxidation process. Excellent wear resistance can be obtained when the amount of silica used is 40 wt.% or more. However, when more than 60 wt.% silica is used, the effectiveness of the catalyst components is diluted by the excess silica, which can also greatly reduce the selectivity of the catalyst. The invention catalyst can be prepared by three successive steps, namely, (1) by preparing a slurry of the starting materials, (2) spray drying the slurry, then (3) firing the dried slurry so obtained.

[0012] It is advisable to use all the components of the catalyst according to the present invention in the form of water-soluble or nitric acid-soluble salts. Ammonium heptamolybdate can be used as the source of molybdenum. The bismuth, iron, nickel, chromium, indium, manganese, zinc, cerium, and sodium can be obtained from the respective nitrates. Phosphoric acid can be used as the source of phosphorus. A silica sol can be used as the source of silica, however it is advisable to prepare this sol with high-purity silica that contains as little aluminum as possible.

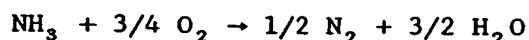
[0013] The slurry of starting materials can be prepared successively by adding phosphoric acid, followed by the addition of an aqueous solution of ammonium heptamolybdate to a silica sol with stirring, then a mixed solution of the nitrates of the other components can be added. The pH of the slurry of starting materials is typically less than 2. Under these conditions, a catalyst with excellent physical properties can be obtained. Next, the slurry of the starting materials can be spray-dried to obtain spherical fine particles that are suitable for use in a fluidized bed reactor.

[0014] Before firing the spray-dried particles, it is advisable to carry

out a denitration process. For example, this denitration can be carried out at 350–450°C for 0.5–2.0 hours, then the denitrated material is fired at 500–650°C, and preferably at 550–630°C, to obtain the catalyst. If the catalyst firing temperature is too low, even though the propylene or isobutylene reactivity may be high, the selectivity for acrylonitrile or methacrylonitrile will be decreased and the wear resistance of the catalyst itself will be lowered. Conversely, if the catalyst firing temperature is too high, the propylene or isobutylene reactivity will be decreased and the combustion of ammonia according to the following equation will be increased:

[0015]

[Equation 1]



The suitable firing temperature for the catalyst of the present invention can be determined from the results of ammoxidation tests at the above-mentioned 500–650°C. A typical firing time is 1–5 hours.

[0016] It is not necessary to use high-purity propylene, isobutylene, and ammonia as the starting materials. For example, industrial-grade starting materials can be used. What is more, tertiary butanol may be used in place of isobutylene, and air is generally used as the source of oxygen. The volume ratio of ammonia and air to propylene or isobutylene is 1:0.9–1.3:7–11, and preferably 1:1.0–1.2:8–10.

[0017] A suitable reaction temperature is 400–460°C, and preferably 410–440°C. A suitable reaction pressure is 1–3 atmospheres. And a suitable contact time between the catalyst and the starting gas mixture is 1–8 seconds, and preferably 2–6 seconds.

[0018]



[Actual Examples] Actual examples will now be used to better explain the present invention.

[0019] (Example of Catalyst Preparation) Catalyst 1 with a composition as indicated by the formula below was deposited on 50 wt.% of silica according to the following procedure:

[0020]

[Formula 3]



A solution prepared by dissolving 406.1 g of ammonium heptamolybdate  $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$  in 1,200 g of water was added to 1,667 g of a 30% silica sol with stirring, then a mixture prepared by dissolving 55.7 g of bismuth nitrate  $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ , 139.8 g of ferric nitrate  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ , 419.3 g of nickel nitrate  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , 46.2 g of chromium nitrate  $[\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ , and 3.87 g of potassium nitrate  $[\text{KNO}_3]$  in 600 g of 13% nitric acid was added. The resulting mixture of starting materials was a slurry with a pH of 0.3. This slurry was then sprayed in a centrifugal spraying apparatus equipped with a dish-type rotor arranged at the center of the upper part of the dryer. The air temperature at the inlet of the dryer was 250°C and the temperature at the outlet was maintained at 130°C to carry out the spray-drying of the slurry. The dry powder thus obtained was transferred to a kiln, denitrated at 400°C for 1 hour, then fired at 560°C for 2 hours to obtain a catalyst.

[0021] The same method as that used above was used to prepare Invention Catalysts 2-11 and Comparison Catalysts 1 and 2 with the compositions indicated in Table 1. In the preparation of the catalysts, for the sources of Mo, Bi, Fe, Ni, Cr, K, and  $\text{SiO}_2$ , the same starting materials as those used in

Invention Catalyst 1 were used. When the catalyst constituents included indium, rubidium, cesium, manganese, magnesium, zinc, cerium, sodium, and/or phosphorus, indium nitrate  $[\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$ , rubidium nitrate  $[\text{RbNO}_3]$ , cesium nitrate  $[\text{CsNO}_3]$ , manganese nitrate  $[\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , magnesium nitrate  $[\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , zinc nitrate  $[\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , cerium nitrate  $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ , sodium nitrate  $[\text{NaNO}_3]$ , and phosphoric acid  $[\text{H}_3\text{PO}_4]$  were used. These catalysts were fired at the temperatures shown in Table 1.

[0022]

[Table 1]

TABLE 1. CATALYST COMPOSITIONS. KEY: (a) catalyst number; (b) atomic ratio of the constituents; (c)  $\text{SiO}_2$ , weight%; (d) firing temperature,  $^\circ\text{C}$ ; (e) Actual Example ..... ; and (f) Comparison Example .....

	触媒 (a) 番号	(b) 原 子 比 組 成								重量% (c) $\text{SiO}_2$	焼 成 (d) ( $^\circ\text{C}$ )
		Mo	Bi	Fe	Ni	Cr	In	A	E		
(e) 実施例	1	12.0	0.6	1.8	7.5	0.6	—	K0.2	—	50.0	560
	2	12.0	0.6	1.8	7.5	—	0.6	K0.2	—	50.0	570
	3	12.0	0.6	2.0	7.5	0.2	0.2	K0.2	—	50.0	580
	4	12.0	0.6	1.8	7.5	0.2	0.4	K0.2	—	50.0	570
	⑤	13.0	0.6	1.8	5.5	0.2	0.4	K0.1Cs0.2	Mn2.0	50.0	600
	6	12.0	0.6	1.4	7.5	0.5	0.5	K0.2	—	50.0	560
	7	12.0	0.6	0.8	7.5	0.6	0.8	K0.2	—	50.0	560
	8	12.0	0.6	1.8	5.5	0.2	0.4	K0.2	Mg2.0	50.0	570
	9	12.5	0.6	1.8	6.5	0.2	0.4	Rb0.2	Zn1.0	50.0	560
	10	12.0	0.4	1.8	7.5	0.2	0.4	K0.2	Ce0.2	50.0	580
	⑪	12.5	0.8	1.8	7.5	0.2	0.6	K0.4	P0.2Na0.1	50.0	620
(f) 比較例	①	12.0	0.6	2.4	7.5	—	—	K0.2	—	50.0	570
	2	12.0	0.6	1.8	7.5	0.2	0.4	—	—	50.0	590

(Actual Example of the Ammoxidation of Propylene) 50 cm<sup>3</sup> of catalyst 1 was put in a vycor glass fluidized bed reaction tube (inner diameter = 25 mm) containing 12 10-mesh metal nets placed at 1-cm intervals. At a reaction temperature of 435°C and a reaction pressure of 1 atmosphere, a gas mixture containing 9 volume% propylene (volume ratio of propylene:ammonia:oxygen:helium = 1:1.2:1.85:7.06) was passed through at a volume flow rate of 3.50 cm<sup>3</sup> per second (converted to STP). The reaction results were expressed in terms of propylene conversion, selectivity for acrylonitrile, and yield of acrylonitrile as determined by the following equations. The actual results obtained are given in Table 2.

[0023]

[Equation 2]

Conversion of Propylene (C) = 100 × moles of propylene consumed/moles of propylene supplied.

Selectivity for Acrylonitrile (S) = 100 × moles of acrylonitrile formed/ /moles of propylene consumed.

Yield of Acrylonitrile (Y) = 100 × moles of acrylonitrile formed/moles of propylene supplied.

The same reaction as the one described above was carried out using Invention Catalysts 2, 3, 4, 6, 7, 8, 9, and 10 and Comparison Catalysts 1 and 2. These reactions were carried out using 9 vol.% of propylene in the starting gas mixture, a volume ratio of ammonia to propylene of 1:1.2, and a volume ratio of oxygen to propylene of 1.8–1.9. Depending on the propylene reactivity of each catalyst, the reaction temperature and contact time as determined by the following formula were adjusted accordingly. The reaction conditions for each catalyst and the reaction results are shown in Table 2.

[0024]

[Equation 3]

$$\text{Contact Time (s)} = V / [F \times (273 + T)/273]$$

where V = amount of catalyst, cm<sup>3</sup>

F = flow rate of starting gas mixture, cm<sup>3</sup> - STP/s

T = reaction temperature, °C

[0025]

[Table 2]

TABLE 2. AMMOXIDATION OF PROPYLENE. Pressure = standard pressure; gas = C<sub>3</sub>H<sub>6</sub>:NH<sub>3</sub>:O<sub>2</sub>:He = 1.0 (9.0%):1.20:1.8-1.9: remainder. KEY: (a) catalyst number; (b) temperature, °C; (c) contact time, s; (d) conversion, %; (e) selectivity, %; (f) yield, %; (g) Actual Example .... ; and h) Comparison

Example	<i>Cat</i> #	<i>Temp.</i> (°C)	<i>C.T.</i> (sec)	O <sub>2</sub> /C <sub>3</sub> H <sub>6</sub>	<i>% conv</i> (d) (%)	<i>Sel</i> (e) (%)	<i>Yld</i> (f) (%)
	触媒 (a) 番号	温度 (b) (°C)	接触 時間(c) (sec)		転化率 (d) (%)	選択率 (e) (%)	収 率 (f) (%)
(g) 実施例	1	435	5.5	1.85	98.5	86.5	85.2
	2	435	5.5	1.85	98.7	86.5	85.4
	3	430	5.0	1.85	98.7	87.1	86.0
	4	430	5.0	1.85	98.8	98.0	86.8
	6	435	5.5	1.85	98.5	87.6	86.3
	7	435	5.5	1.85	98.3	87.6	86.1
	8	430	5.5	1.85	98.6	87.7	86.5
	9	430	5.5	1.88	98.2	87.5	85.9
	10	425	5.0	1.88	99.0	86.9	86.0
(h) 比較例	1	430	5.0	1.88	98.5	85.4	84.1
	2	420	4.8	1.90	99.6	82.9	82.6

(Actual Example of the Ammoxidation of Isobutylene) 50 cm<sup>3</sup> of Invention Catalyst 5 was put in the reaction tube used in the above-mentioned ammoxida-

tion of propylene. At a reaction temperature of 430°C and standard pressure, a gas mixture containing 7.5 vol.% isobutylene (isobutylene:ammonia:oxygen:oxygen:water:helium = 1:1.2:1.95:1.8:7.38) was passed through the reaction tube at a flow rate of 3.88 cm<sup>3</sup> (converted to STP) per second. The reaction results were expressed in terms of isobutylene conversion, selectivity for methacrylonitrile, and yield of methacrylonitrile, as determined above for propylene. The actual results obtained are given in Table 3.

[0026] The above-mentioned reaction was carried out using Invention Catalyst 11 and Comparison Catalyst 1. The reaction conditions for each catalyst and the reaction results are given in Table 3.

[0027]

[Table 3]

TABLE 3. AMMOXIDATION OF ISOBUTYLENE. Pressure = standard pressure; gas = C<sub>4</sub>H<sub>8</sub>:NH<sub>3</sub>:O<sub>2</sub>:He = 1.0 (7.5%):1.20:1.9-2.0:1.8:the remainder. KEY: (a) catalyst number; (b) temperature, °C; (c) contact time, s; (d) conversion, %; (e) selectivity, %; (f) yield, %; (g) Actual Example .... ; and (h) Comparison Example ....

	触媒 (a) 番号	温度 (b) (°C)	接触 時間(c) (sec)	O <sub>2</sub> /C <sub>4</sub> H <sub>8</sub>	転化率 (d) (%)	選択率 (e) (%)	収率 (f) (%)
(g) 実施例	5	430	5.0	1.95	99.5	79.6	79.2
	11	430	5.0	1.95	99.7	79.2	79.0
(h) 比較例	1	430	5.0	1.95	99.7	77.0	76.8

[0028]

[Effect of the Invention] According to the present invention, by using a catalyst prepared by blending oxides of specific metal components with a catalyst component that contains molybdenum, bismuth, and iron for the ammoxidation of propylene or isobutylene, the yield of acrylonitrile or methacrylonitrile can be improved considerably.